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Anthocyanins in grapes and wines: old, new and recurring chemical problems

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The anthocyanins present in grapes and wines have been the subject of extensive research. In July 2015, over 4000 documents can be recovered by the ISI-WoS database with the simple search: TS=(anthocyan* AND (grape* OR wine*)). Since 2012, more than one ISI research product per day has been released into the public domain. In this rapidly changing context, the aim of this presentation is to compile a tentative list of old and new chemical problems with the potential to have an impact on the wine economy.

A long-standing problem in viticulture is the production of resistant, qualitatively sound grapevine hybrids with a substantial majority of *V. vinifera* DNA. Old and new data support the hypothesis that a concerted effort should be made to accelerate the transfer of results from anthocyanin research to the release of new resistant cultivars free from the excessive presence of anthocyanin-3,5-diglucosides in the berry.

Another widely discussed problem is the potential transfer of several successful applications of anthocyanin profiles to grape chemotaxonomy for the discrimination of monovarietal wines, including aged red wines. A possible answer comes from consideration of the extensive profile of wine pigments measured using LC-MS/MS, and not only of native grape anthocyanins [1]. While feasible for research purposes, the need to calibrate mass spectrometers with pure standard still makes this kind of investigation expensive and to date impractical for wide application in many laboratories.

Another potentially underexplored field is the study of the factors influencing the pattern and concentration of wine pigments. Micro-oxygenation before malolactic fermentation modulates not only grape anthocyanins, but also several pigments formed during wine ageing, including vitisins, vinylphenol-pyranoanthocyanins and the products of both direct and indirect reactions between anthocyanins and flavanols [2]. The domestic storage of red wines has been found to induce an accelerated decrease in wine pigments, while specifically promoting the formation of pinotin A-like pigments [3]. We can therefore suggest that oxygen management and storage temperature have the potential to modify the relative percentages of wine pigments, affecting wine colour and quality.

Moreover, the use of LC-MS/MS in targeted metabolomics has led to discovery of the presence of minute amounts of anthocyanins and wine pigments in white grapes [4]. This finding, which could be regarded as a curiosity, actually has practical implications for grape taxonomy. It calls for the need to define the analytical threshold, the concentration of anthocyanins below which a cultivar can be classified as "white", since widely accepted qualitative discrimination based on presence/absence no longer complies with the analytical sensitivity assured by modern tandem mass spectrometers.

References

[1] Arapitsas P., Perenzoni D., Nicolini G., Mattivi F. Study of Sangiovese wines pigment profile by UHPLC-MS/MS. *Journal of Agricultural and Food Chemistry*, **2012**, <u>60</u>, 10461-10471.

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^[2] Arapitsas P., *et al.* A metabolomic approach to the study of wine micro-oxygenation. *Plos ONE*, **2014**, <u>7</u>(5), e37783.